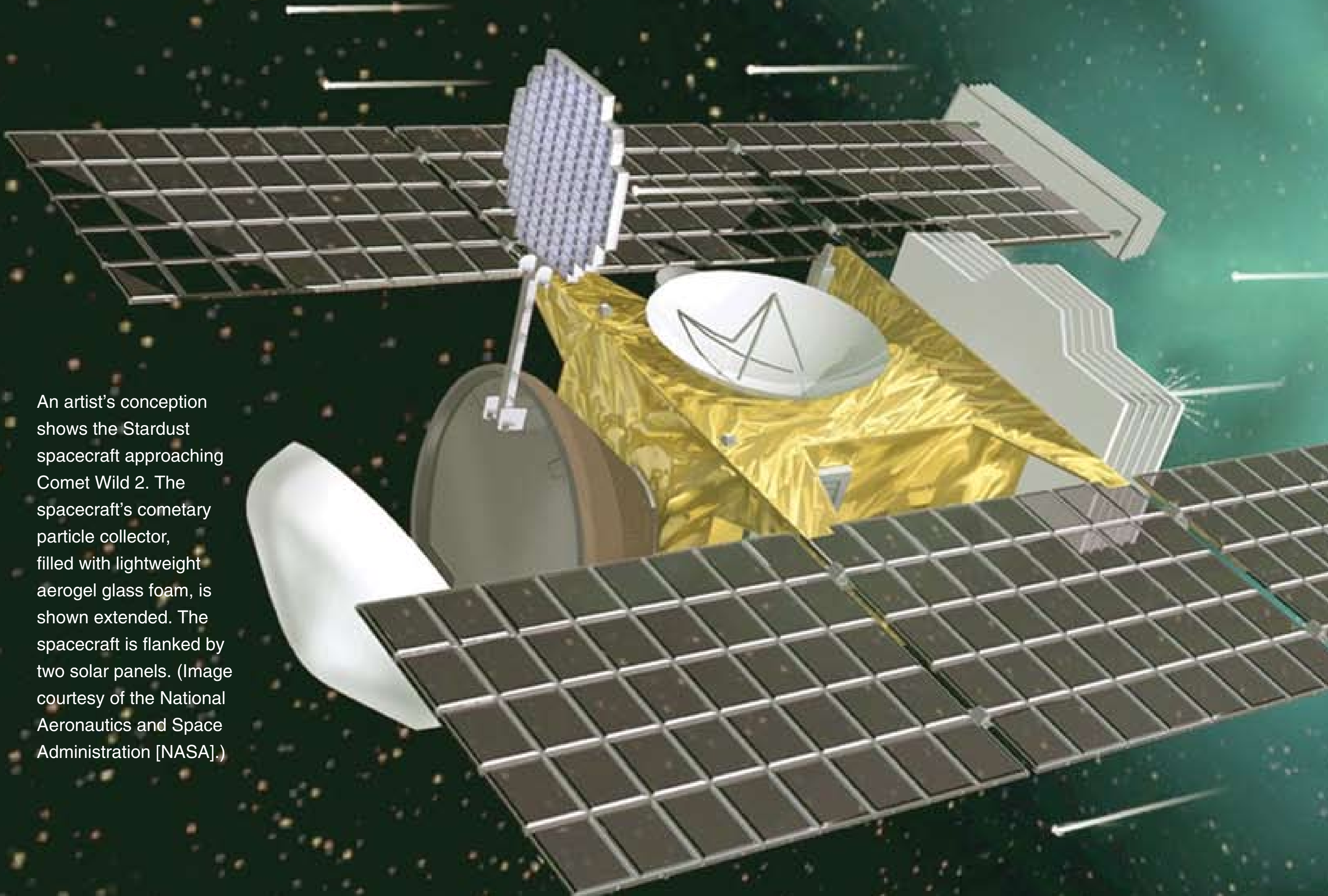
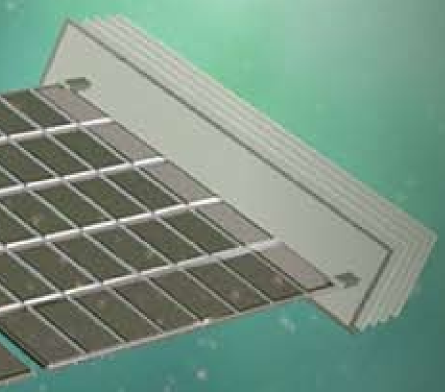


An artist's conception shows the Stardust spacecraft approaching Comet Wild 2. The spacecraft's cometary particle collector, filled with lightweight aerogel glass foam, is shown extended. The spacecraft is flanked by two solar panels. (Image courtesy of the National Aeronautics and Space Administration [NASA].)

Stardust Results Challenge

Astronomical Convention

A Livermore team has discovered plenty of surprises in the first samples captured from a comet.



FORMED in the frozen reaches of the solar system beyond the outer planets, comets have been considered the oldest, most primitive bodies in the solar system. They were thought to be composed of preserved interstellar particles from 4.6 billion years ago, when the Sun and the planets began to form from a primordial disk of dust and gas. However, the first-ever study of material retrieved from a comet is giving scientists, including a team of Lawrence Livermore researchers, new and sometimes startling insights into the makeup of comets and clues that the early solar system was far more active than previously believed.

The particles under intense study were captured in 2004, when the National Aeronautics and Space Administration's (NASA's) Stardust spacecraft flew through the tail of a comet called Wild 2 (pronounced "Vilt 2" after the name of its Swiss discoverer) as it neared the orbit of Mars. As Stardust approached the 4.5-kilometer-diameter comet, the spacecraft briefly extended a collector filled with lightweight aerogel glass foam to safely capture thousands of tiny particles. With its collector stowed, the spacecraft then sped close to Earth and on January 15, 2006, ejected its sample return capsule safely onto the Utah desert southwest of Salt Lake City.

Stardust, which is the first U.S. spacecraft to return solid space samples to Earth since the Apollo lunar missions, also collected dust from a flow of particles that pass through our solar system from interstellar space. Stardust's precious preserved cargo weighed less than 1 milligram; yet, this cometary material is providing more than enough samples to keep hundreds of investigators worldwide busy for decades to come.

The 13-member Livermore team, headed by physicist John Bradley, director of Livermore's Institute of Geophysics and Planetary Physics (IGPP), and Ian Hutcheon, deputy director of the Glenn T. Seaborg Institute, has been feverishly examining some of the particles since shortly after the sample return capsule parachuted to Earth. The team's preliminary data, together with those gathered by their colleagues, were presented in December 2006 at the American Geophysical Union's meeting in San Francisco, California. The results were simultaneously published in the December 15, 2006, issue of *Science*. Livermore researchers were coauthors

John Bradley gives the thumbs-up sign after scientists opened the Stardust sample return capsule in the clean room facility at NASA's Johnson Space Center. In the background, researchers photograph the particle collector filled with aerogel cells that trapped tiny cometary particles.

on all seven *Science* papers detailing the first findings.

The Livermore team includes Giles Graham, Hope Ishii, Zurong Dai, Saša Bajt, Patrick G. Grant, Jerome Aleon (now at Centre de Spectrometrie Nucleaire et de Spectrometrie de Masse in France), Alice Toppani (now at Centre National de la Recherche Scientifique in France), Peter Weber, Stewart Fallon (now at Australian National University), Nick Teslich, and Miaofang Chi. The researchers are from Livermore's Physics and Advanced Technologies; Chemistry, Materials, and Life Sciences (CMLS); and Energy and Environment directorates. The Livermore work is part of the Bay Area Particle Analysis Consortium (BayPAC) established in 2003 to maximize the strengths of San Francisco Bay Area research facilities for examining Stardust particles. BayPAC was recently expanded into the West Coast Consortium with the inclusion of the University of California (UC) at Los Angeles and the University of Washington. Other members include NASA/Ames Research Center, UC Berkeley, Lawrence Berkeley National Laboratory, Stanford Linear Accelerator Center, and UC Davis.

Researchers have long wanted to study cometary samples and determine their chemistry, mineralogy, crystal structure, and trace-element and isotope compositions. The analyses by Livermore and other scientists are providing important new data about the formation of the solar system as well as comets. Preliminary studies show that Comet Wild 2 contains an impressive assortment of materials, many unexpected. In particular, the comet contains an abundance of high-temperature minerals that appear to have formed in the inner regions of the solar nebula. Their unexpected presence strongly suggests that the formation of the solar system included mixing over radial distances much greater than has been generally accepted by scientists in the past.

In the early 1990s, with funding from NASA and the Jet Propulsion Laboratory

The Stardust Mission

The Stardust spacecraft was launched February 7, 1999, embarking on a flight path of three giant loops around the Sun. On January 2, 2004, the spacecraft met Comet Wild 2 beyond the orbit of Mars. While flying through the dust cloud surrounding Wild 2, the spacecraft flipped open a tennis racket–shaped collector that was stashed inside the protective sample return capsule.

The particles impacted the collector at about 6.1 kilometers per second (six times faster than a bullet fired from a gun), but the collector's aerogel cells cushioned their impact and lessened the damage. The spacecraft also recorded in-flight data with its mass spectrometer and particle counter and took detailed pictures of Wild 2's surface, the best photos ever taken of a comet nucleus. The collector then folded down into the capsule, which enclosed the samples for safe delivery to Earth.

The collector had two nearly identical sides. One side of the collector faced toward the particles streaming off Wild 2 in 2004, while the reverse side, with a second set of aerogel cells, was turned earlier to face the streams of smaller interstellar dust particles encountered from March through May 2000.

Comets are relatively small, irregularly shaped bodies that spend most of their existence in the outer reaches of the Sun's influence, which is why so much of their original material is well preserved. When a comet approaches within about 700 million kilometers of the Sun, material on the comet's nucleus heats and begins to vaporize. This phenomenon creates a cloud of dust and ionized gas called the coma and a tail of gases that flows millions of kilometers beyond the nucleus.

Wild 2's nucleus, which measures about 4.5 kilometers in diameter, was probably formed in the Kuiper Belt, far beyond Neptune. Over many millions of years, the comet slowly ventured into the inner solar system, where it had a close encounter with Jupiter in 1974. This encounter placed the comet in its current orbit between Mars and Jupiter, making it an ideal candidate for a National Aeronautics and Space Administration (NASA) mission. Because Wild 2 has not traveled close to the Sun for long, its composition has not changed substantially since its formation billions of years ago.

The Stardust spacecraft is currently orbiting the Sun. NASA is considering a proposal that the spacecraft be sent to fly by Comet Tempel I. In 2005, another NASA spacecraft, Deep Impact, launched an impactor that struck Tempel I and revealed its inner nucleus. With the prospect of visits by future missions, comets will continue to help unravel secrets of the solar system.

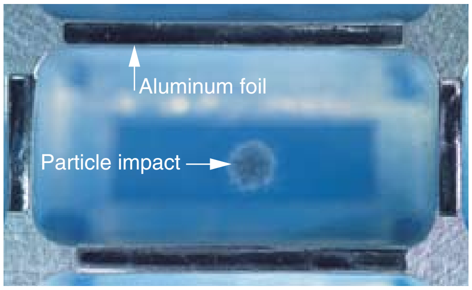
This image of Comet Wild 2 was taken by NASA's Stardust spacecraft on January 2, 2004. The nucleus of the comet (shown here) without its million-kilometer-long tail measures about 4.5 kilometers in diameter. (Image courtesy of NASA/Jet Propulsion Laboratory–California Institute of Technology [JPL–Caltech].)

(JPL), which manages the Stardust mission, Livermore scientists from the CMLS Directorate developed methods to produce the ultralow-density silica aerogel for Stardust. For more than two decades, Livermore researchers have pioneered the formulation and application of silica aerogels, an extremely lightweight glassy material with ideal mechanical characteristics for capturing ultrafast particles.

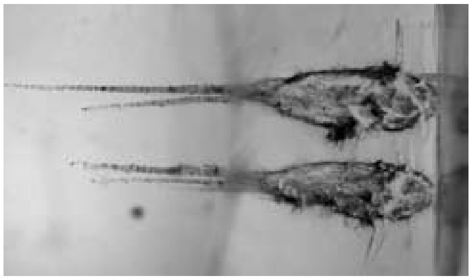
In the late 1990s, physicist Dai, while still at Georgia Institute of Technology, and Bradley used electron microscopes to image interplanetary dust particles captured in Earth's stratosphere by NASA's ER-2 aircraft. At Livermore, Bradley was the principal investigator for a Laboratory Directed Research and Development–funded project to develop technologies for analyzing cometary material from aerogels. As part of this effort, physicist Bajt developed new techniques to characterize particles captured in the stratosphere as well as particles collected by the NASA Orbital Debris Collection Experiment from Russia's Mir Space Station. At the same time, physicist Graham was working with a group in the United Kingdom to conduct experiments that would examine the tracks formed by simulated cometary particles fired at ultrahigh speeds into aerogels.

Working at Johnson Space Center

Livermore researchers were on hand when the sample return capsule arrived at NASA's Johnson Space Center in Houston. The sample tray with aerogel cells was opened in a clean room similar to that used in the semiconductor industry. The 132 aerogel cells, each measuring 2 by 4 by 3 centimeters and mounted in an aluminum structure, appeared largely intact. In fact, so pristine was the collector's appearance, more than one observer worried that it might not have deployed. On closer observation, the researchers made out hundreds of particle impact tracks within each cell. The particles fragmented extensively as they traveled into the aerogel. The tracks measured up to 2 centimeters long, and up to half a centimeter in diameter, and each one contained dozens of tiny particle fragments. Most were smaller than 10 micrometers in diameter, but the largest was visible to the naked eye. Many particles were captured in good condition, although some were coated with a thin layer of melted aerogel.



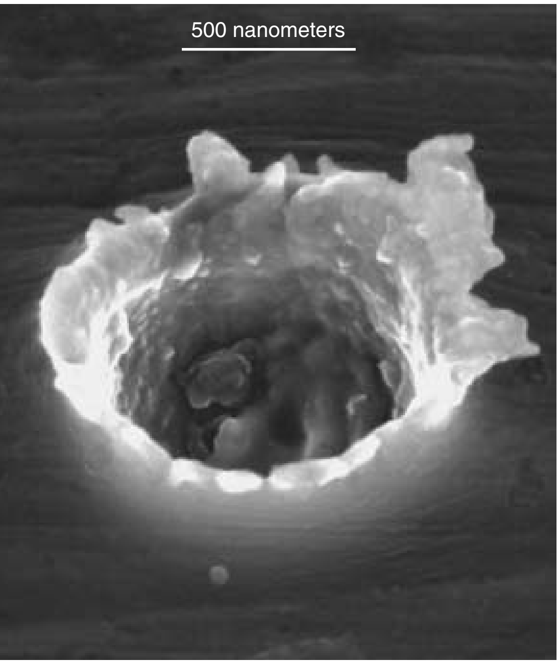
A close-up view shows a trapped cometary particle in an aerogel cell shortly after Stardust's sample return capsule was opened. Also visible is aluminum foil wrapped around the collector grid walls. (Image courtesy of NASA/JPL–Caltech.)



A photo shows tracks left by two cometary particles trapped by aerogel in the collector grid as they entered from the right. The tracks are magnified several hundred times. (Image courtesy of NASA/JPL–Caltech.)

During a heavily attended press conference at Lawrence Livermore, materials scientist Hope Ishii shows reporters a recently returned sample of aerogel containing cometary particles. The plastic barrier protects the sample from contamination.

Livermore played a major role in developing particle extraction technologies adopted by NASA. At the Johnson Space Center, IGPP personnel assisted in some of the first extractions using a tiny knife developed by Ishii, a materials scientist. The knife has a diamond blade that vibrates at ultrasonic frequency to make smooth cuts in aerogel, a difficult task because the brittle material is prone to breaking. The ultrasonic knife is one of several aerogel cutting tools developed to extract cometary particles at the center. Microneedles were also used to extract wedge-shaped aerogel slices called keystones. Each keystone contained an intact particle track. A silicon "microfork" was then used to remove the keystones for further analysis. Both the microneedles and microfork were developed at UC Berkeley.



A scanning electron microscope image shows an impact crater preserved on the surface of a foil.

Many keystones and some of the extracted individual cometary particles were embedded in epoxy, then cut into extremely thin sections with an ultramicrotome stationary diamond blade. Bradley pioneered the use of ultramicrotomy for sectioning extraterrestrial particles in the mid-1980s. Both keystones and isolated particles were distributed to Livermore and other research laboratories around the world. As part of the Stardust Preliminary Examination, samples are often forwarded from one research center to another. For example, the Livermore team has received samples from several centers with the request that Laboratory researchers corroborate or amplify findings.

Some Wild 2 particles were also caught in the high-purity aluminum foils that wrapped around the particle collector's aluminum structure and provided additional security for the aerogel cells. The impacts on the foils produced bowl-shaped craters lined with particles. Graham and Teslich were among the first scientists to detect the craters containing miniscule particles in the collector foils. They used Livermore's focused ion beam to mill away small areas of foil and cut out particle cross sections.

"We thought all the particles caught in the foils would be melted on impact, but some appear to have survived relatively intact," says Graham. "They are proving as important as those caught in the aerogel cells." He notes that particles caught in the foils are localized in the minuscule craters, whereas particles caught in the aerogel cells are arrayed along a track. As a result, the foil-trapped particles are more easily accessed than the particles embedded in aerogel. The foil-trapped particles also are not exposed to contamination from the silicon and oxygen in the melted aerogel.

Advanced Instruments Put to Work

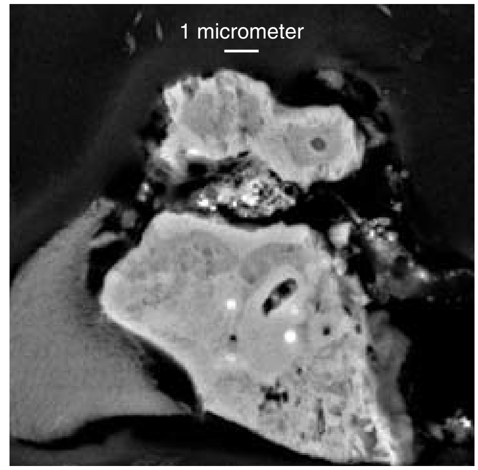
Livermore scientists are characterizing particles extracted from both aerogel and foil with highly specialized instruments such as the super scanning transmission electron microscope (SuperSTEM), nanometer-scale secondary-ion mass spectrometer (NanoSIMS), scanning electron microscope (SEM), and nuclear microprobe. The ability to carry out correlated studies on individual micrometer-size grains using multiple analytic tools is a unique strength of the Livermore team. The researchers also use the infrared microspectroscopy beam line at the Advanced Light Source at Lawrence Berkeley and the x-ray microprobe at the Stanford Synchrotron Radiation Laboratory, a part of the Stanford Linear Accelerator Center.

The highest spatial resolution work is being done using SuperSTEM, the world's most powerful electron microscope. SuperSTEM allows atomic-scale analyses of a particle's composition and produces stunning pictures magnified several million times. The machine has ancillary equipment that corrects images for blurring, yielding striking pictures of a mineral's crystalline structure. "SuperSTEM is invaluable because some of the most significant information contained in the Stardust samples is at the atomic scale," says Bradley.

"We see an extensive variation both from particle to particle and from area to area within each particle on SuperSTEM," says Dai. "In particular, we are seeing many silicate minerals."

Work on SuperSTEM is complemented with a new field-emission SEM, which produces images at magnifications up to about 1 million times. Electrons pass through the sample with SuperSTEM but bounce off the sample with field-emission SEM, yielding different but just as

Zurong Dai uses a transmission electron microscope to take close-up images of cometary dust particles extracted from the aerogel cells.



A scanning electron microscope image shows a calcium aluminum-rich inclusion particle found in a Stardust sample. The particle is made up of several high-temperature minerals. The contrast in the image is caused by differences in atomic weight of the atoms present. Some aerogel is adhered to the particle on the lower left corner.

valuable images. According to Hutcheon, who is chief scientist for Livermore's Forensic Science Center, the SEM is a valuable complement to SuperSTEM because it enables visualization of textural relationships between different minerals.

NanoSIMS is used for the chemical and isotopic analysis of extremely small volumes of material. The machine examines material a few micrometers in diameter and 1 to 2 micrometers in depth. It uses an ion beam (typically oxygen or cesium) to produce plasma of the target material. (See *S&TR*, January/February 2007, pp. 12–20.) Determining the isotope ratios of several key elements has been critical for proving that many of Wild 2's minerals were created close to the Sun.

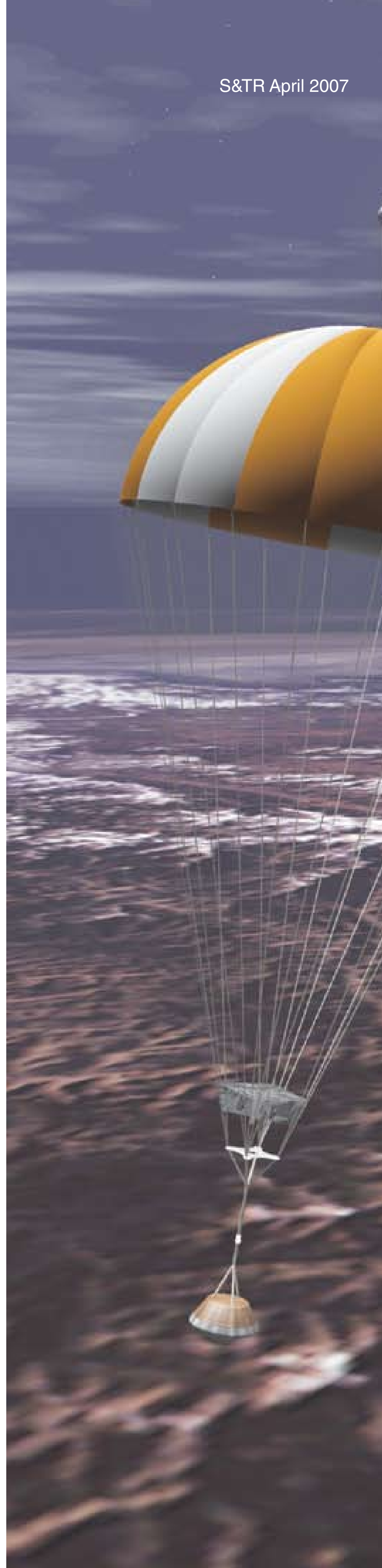
Ishii is using the x-ray microprobe at the Stanford Synchrotron Radiation Laboratory for generating extremely bright x rays to map the distribution of elements along intact tracks cut out of an aerogel cell. These data contribute to bulk composition estimates for Comet Wild 2 as well as guide future studies on a given impact track. Entire tracks are also analyzed at Livermore's Center for Accelerator Mass Spectrometry. At the center, chemist Grant examines tracks with a nuclear microprobe, which uses a proton beam. Other analysis techniques include scanning transmission ion microscopy, proton elastic scattering, proton backscattering, and proton-induced x-ray emission. Together, these techniques enable Grant to measure the total mass of the particles as well as the elements contained in the particles and tracks.

Bajt uses the Advanced Light Source's infrared microspectroscope to analyze the same small, thin sections required by SuperSTEM as well as entire keystones. The technique uses an intense infrared beam from the synchrotron.

Full of Surprises

"The particles are full of surprises," says Bradley. "They are a remarkable mixture of materials. The biggest surprise is that although comets were formed a long distance from the Sun, far beyond the orbit of Neptune, Wild 2 appears to be full of material from the inner solar system and from close to the Sun. These findings are not what we expected." Extraterrestrial dust particles previously collected in the stratosphere were thought to mostly consist of particles from comets. However, says Bradley, "Wild 2 particles don't look anything like the particles we have captured in the upper atmosphere and have believed to be cometary in origin. In this case, we're seeing large variations from particle to particle."

Another surprise is the scarcity of presolar material, the tiny interstellar grains produced around other stars that existed before the Sun and solar system formed. Except for a single 250-nanometer-diameter grain highly enriched in oxygen-17, the mineral grains have isotopic compositions similar to typical solar system material. However, Wild 2 is full of complex minerals, many of which form only at very high temperatures, presumably near the Sun. For example,



a calcium aluminum–rich inclusion has been identified. This inclusion is believed to have been created in the hottest, innermost regions of the gas and dust disk that formed the Sun and planets. Calcium aluminum–rich inclusions are also found in meteorites formed in the asteroid belt. “Calcium aluminum–rich inclusions shouldn’t be there,” says Hutcheon. “They are the last thing we expected to find.” The Livermore team, using the field-emission SEM, provided NASA with a rigorous characterization of the inclusion.

Other high-temperature minerals include olivine and pyroxene (magnesium iron silicates), both associated with igneous rocks on Earth. Olivine is the primary component of the green sand found on some Hawaiian beaches and is among the most common crystalline minerals in the galaxy.

Miaofang Chi, a Student Employee Graduate Research Fellowship participant from UC Davis, performed much of the work using SuperSTEM on the calcium aluminum–rich inclusions to identify osbornite (titanium nitride). “Osbornite is a mineral that forms at about 3,000 kelvins, which means it formed close to the hot, infant Sun,” says Chi.

Wild 2’s high-temperature minerals were apparently transported from near the Sun to the outer regions of the solar system by a process capable of moving particles at least as large as 20 micrometers, the size of some of the mineral inclusions. The inescapable conclusion is that vastly more mixing of material occurred while the Sun and planets were forming than scientists expected. “The conventional thinking was that the formation of the solar system as we know it was a rather quiet, orderly process,” says Ishii. “However, it now appears that the early solar system was a much more dynamic and violent environment than we thought.”

The discovery of high-temperature (refractory) minerals supports the theory proposed in the 1990s that large particles could have been transported by the so-called X-wind from a region surrounding the young Sun. The wind supposedly flowed perpendicular to the disk of hot dust and gas forming the Sun and planets and shot material out hundreds of millions of kilometers in an X shape. Some of the material in the X-wind may have rained into the comet-forming region where it was incorporated into Comet Wild 2.

Rich Diversity of Carbon Compounds

Many of the particles studied thus far contain organic compounds that are surprisingly diverse. The presence of organic compounds in comets is of interest to astrobiologists because the organic precursors of life on Earth may have come from a comet.

Using an infrared microscope at the Advanced Light Source, Bajt detected carbon-rich materials and was the first to chart the distribution of organic compounds along aerogel tracks in a keystone. “Infrared is especially sensitive to organic molecules,” Bajt says. “We didn’t expect organics to survive the impact with the aerogel during the collection process.” However, she found more diversity of organic compounds that were both oxygen- and nitrogen-rich compared with organics identified on the flyby of the Halley Comet, which had an onboard mass spectrometer. Many organic compounds volatilized during impact and diffused into the surrounding aerogel, where they remain.

The comet’s organic materials might be more primitive than those seen in meteorites and might have formed in clouds between the stars or in the disk-shaped cloud of gas and dust from which our solar system formed. They may represent a new class of organic compounds not previously observed in other extraterrestrial samples,

Stardust's sample return capsule parachutes to Earth. (Image courtesy of NASA.)

including meteorites and interstellar dust particles.

Bajt notes that infrared spectroscopy allows scientists to image objects exactly as astronomers see them. In this way, her research provides "ground truth" for images of comets, such as Wild 2, taken with infrared terrestrial and space telescopes. Distinguishing carbon contaminants from cometary materials is also important. For example, aerogel consists predominantly of silicon dioxide but also contains a small amount of carbon. However, aerogel carbon is in the form of simple silicon-methyl groups, which are different from the organic compounds found on Wild 2.

Future Plans Look Bright

More than 90 percent of the collected matter remains locked in the aerogel and aluminum foils, archived at Johnson Space Center and stored in dry nitrogen for future researchers. The Livermore team is preparing a second set of papers for publication that will have more detailed results than the initial results published in *Science*.

When the spacecraft was launched in 2004, many of the analytic techniques being used to examine Wild 2 particles didn't exist. "We expect new techniques to come along over the next few years that will provide important additional information," Bradley says. As data accumulate, the results will permit a thorough comparison with samples from asteroids, believed to have been formed in the warmer, inner regions of the solar system, and with interplanetary dust collected from Earth's stratosphere.

The Livermore team is looking forward to analyzing interstellar particles, which were collected by less-dense aerogel cells on Stardust than those that collected Wild 2 particles. In the meantime, an online project called Stardust@Home (http://stardustathome.ssl.berkeley.edu) gives members of the public the opportunity to examine close-up images of the aerogel cells for signs of the dust trails left by interstellar particles, which are smaller than those from Wild 2.

The advanced techniques applied to the Stardust samples have direct benefits to many Livermore programs. For example, the ultrasonic diamond-blade technology developed by Ishii has potential application to other Livermore programs that use aerogels in experiments. In addition, the techniques used to investigate Stardust samples are used to interrogate interdicted materials for nuclear forensic science in support of nonproliferation and national security. Increased expertise with the analytic instruments aids both causes. Bradley says, "The work has been a great example of collaboration across directorates at the Laboratory and has nicely showcased Livermore's superb analytic capabilities. In addition, our Stardust effort has attracted many outstanding young scientists to Livermore who are excited by the rare opportunity to do research on extraterrestrial matter with world-class equipment."

"The Stardust mission has been a stunning success, far exceeding even our most optimistic expectations," Bradley says. Adds Ishii, "This is the opportunity of a lifetime."

—Arnie Heller

Key Words: Advanced Light Source, aerogel, Bay Area Particle Analysis Consortium (BayPAC), Center for Accelerator Mass Spectrometry, Comet Wild 2, Institute of Geophysics and Planetary Physics (IGPP), nanometer-scale secondary-ion mass spectrometer (NanoSIMS), scanning electron microscope (SEM), Stanford Synchrotron Radiation Laboratory, Stardust spacecraft, super scanning transmission electron microscope (SuperSTEM), X-wind.

For further information contact John Bradley (925) 423-0666 (bradley33@llnl.gov).